

**The Rovibrational Intensities of the  
2V<sub>3</sub> Band of <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O at 4639 cm<sup>-1</sup>**

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**PROPOSED RUNNING HEAD**  
**INTENSITIES OF  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$   $2\nu_3$  BAND**

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## INTRODUCTION

Recent studies involving intensity measurements of weak CO<sub>2</sub> bands in the near-infrared<sup>1-2</sup> were undertaken primarily to provide improved absorption parameters to model the night-side emission spectrum of Venus. Measurement of the intensity of some of these bands also provides the basis for improving the theoretical computation of many weaker CO<sub>2</sub> bands that cannot be measured. The hot, extensive atmosphere of Venus is primarily CO<sub>2</sub>, so many bands that are weaker than are listed in the HITRAN compilation<sup>3</sup> are needed for complete modeling of Venus' atmosphere. For most CO<sub>2</sub> bands, intensity measurements need only be made for the major isotope <sup>12</sup>C<sup>16</sup>O<sub>2</sub>, which could provide the basis for calculating the intensities of the corresponding bands of the minor isotopes. However, some transitions are forbidden in the symmetric isotopomers <sup>12</sup>C<sup>16</sup>O<sub>2</sub> and <sup>13</sup>C<sup>16</sup>O<sub>2</sub>; absorption bands are only observed for these transitions in the asymmetric isotopomers. An important band of this type near the 2.2 μm emission window in Venus' night-side spectrum is the 2ν<sub>3</sub> band of <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O at 4639 cm<sup>-1</sup>.

The strength of this band currently used in the HITRAN compilation<sup>3</sup> was obtained by Abubakar and Shaw<sup>4</sup> using the technique of nonlinear least-squares whole-band analysis. Their two spectra had resolution of 0.06 cm<sup>-1</sup> and signal/noise of 130 and 260. With several spectra available in this wavenumber region that are about 5 times better in both resolution and signal/noise, we expected that measurements of individual lines could improve the intensity parameters of this band. We therefore selected the four spectra on

Line intensities were determined using non-linear least-squares fitting of the spectra<sup>7</sup>. Line broadening coefficients are required for these intensity determinations, but we did not adopt the HITRAN<sup>3</sup> CO<sub>2</sub> self-broadening values. The HITRAN values are based on careful measurements of several <sup>12</sup>C<sup>16</sup>O<sub>2</sub> bands, and are assumed applicable to all bands, regardless of vibrational transition or CO<sub>2</sub> isotopomer. We decided to investigate this assumption for this 2v<sub>3</sub> band since for <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O in normal isotopic abundance, broadening is mostly "foreign" broadening by <sup>12</sup>C<sup>16</sup>O<sub>2</sub>. The latter may be somewhat different from the HITRAN self-broadening values. We therefore included the determination of the "foreign" broadening parameters,  $\gamma_f$ , in the measurements of the best isolated lines on spectrum No. 4; this spectrum was selected because the higher pressure spectrum with sufficiently deep lines should produce the more reliable broadening measurements. These values were then plotted against  $\ln l$  and smoothed; the smoothed values were adopted for intensity fits for all 4 spectra. These smoothed values are presented in the last column of Table 2. They are somewhat smaller (on the order of 3%) than HITRAN self-broadening coefficients at low-J values, but were indistinguishable for  $J > 30$ .

We then determined  $\gamma_f$  parameters in isolated P-branch lines on spectrum No. 2, obtained at 45 torr, to check the reproducibility of our results from spectrum No. 4. The measurements from spectrum No. 2 were in very close agreement with HITRAN values, although we regard them as less reliable than the  $\gamma_f$  parameters from spectrum No. 4. The uncertainties in the  $\gamma_f$  parameters limit the absolute

## DATA ANALYSIS

The measured line intensities in the units of  $\text{cm}^{-1}/(\text{cm-atm})$  for each spectrum were converted to the standard temperature, 296 K, via the relation

$$\frac{S(T)}{S(T')} = \frac{Q_{vr}(T')}{Q_{vr}(T)} \left( \frac{T'}{T} \right) \exp \left[ \frac{-hcE''}{k} \left( \frac{1}{T} - \frac{1}{T'} \right) \right]. \quad (1)$$

The rovibrational partition function values,  $Q_{vr}$ , for  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  were obtained from Gray and Young<sup>9</sup> and the lower state rotational energy values  $E''$  ( $\text{cm}^{-1}$ ) were adopted from the HITRAN<sup>3</sup> tabulation. The intensity values were converted to units of  $\text{cm}^{-1}/(\text{molecule}/\text{cm}^2)$  by dividing by  $2.68676 \times 10^{19}$  ( $273.15/296$ ). The rotationless transition moment squared and Herman-Wallis intensity parameters were obtained from the measured line intensities standardized to 296 K via the theoretical expression for the individual line intensities,

$$S_{J''} = \{8\pi^3 10^{-36} / [3hcQ_{vr}(T)]\} \{ \sigma \exp(-hcE''/kT) \} L_{J''} |R_{vib}|^2 F(m), \quad (2)$$

where the line intensity is in units of  $\text{cm}^{-1}/(\text{molecule}/\text{cm}^2)$ . The square of the rotationless transition moment  $|R_{vib}|^2$  has units of  $\text{Debye}^2$ ,  $J''$  is the lower state rotational quantum number, and  $\sigma$  ( $\text{cm}^{-1}$ ) is the line position. The Hönl-London line strength factors  $L_{J''}$  are equal to  $J''$  and  $(J''+1)$  respectively, for the P and R branches of the  $2\nu_3$  band.  $T$  is the Kelvin temperature and  $k$ ,  $h$  and  $c$  have their usual meanings.

parameters obtained from fitting Eq. 5 above are given in Table 3. Fig. 2 shows the plot of square root of reduced intensities versus  $m$  for each of the four spectra.

The rotationless band strength  $S_{\text{vib}}^0$ , was evaluated at 296 K from the value of the rotationless transition moment:

$$S_{\text{vib}}^0(T) = \{8\pi^3 10^{-36} / [3hcQ_v(T)]\} \sigma_o f |R_{\text{vib}}|^2 \quad (7)$$

using the value of the vibrational partition function,  $Q_v(296\text{K})=1.08724$ , from Gray and Young<sup>9</sup>, and the vibrational band origin,  $\sigma_o=4639.501 \text{ cm}^{-1}$ . This definition of  $S_{\text{vib}}^0$ , which includes the normal isotopic abundance factor  $f$ , follows Rothman et al<sup>3</sup> to be consistent with HITRAN usage. The result is included in Table 3.

## DISCUSSION

The rotationless band strength we have obtained for the  $2\nu_3$  band of  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  in natural  $\text{CO}_2$  is 16% larger than previously determined by Abubakar and Shaw<sup>4</sup> who used the technique of nonlinear least-squares whole-band analysis. The Herman-Wallis parameter that we determined in Table 3 is very small and could not be determined with statistical significance. Therefore, we assumed  $F(m)=1$  in the calculation of  $S_{\text{cal}}$ . The values of  $S_{\text{cal}}$  are given in Table 2. The precision of our intensity measurements, which on average is better than 1% as seen from column 4 of Table 2, takes account of uncertainties in the measurements of temperature and gas pressure in the cell. The relative dispersion of the intensity values as observed from column 6 of Table 2 is less than 1.5% on average.

on  $\gamma_f$  for these spectra with CO<sub>2</sub> pressures of 45 to 65 torr. Therefore, the likely systematic errors in the line intensities, and thus the band intensity, is less than  $\pm 3\%$  from this main source of systematic uncertainties. Then, since  $|R_{vib}|$  is proportional to  $(S_{vib}^0)^{1/2}$ , the likely systematic error associated with  $|R_{vib}|$  is less than  $\pm 1.5\%$ .

Our tabulated line positions are the unweighted averages of the values measured and calibrated on our four spectra, which were obtained with CO<sub>2</sub> pressures from 45 to 65 torr; the average pressure is about 54 torr. These positions are only about 0.0005 cm<sup>-1</sup> smaller than the HITRAN<sup>3</sup> zero-pressure line positions. The HITRAN line positions were calculated from J' upper level rotational constants determined from measurements in the 2v<sub>3</sub>-v<sub>3</sub> band at 2307.4 cm<sup>-1</sup> which HITRAN attributed to M. P. Esplin in 1987. If our line positions and the HITRAN values are both correct, the differences can be attributed to pressure shifts of about -0.007 cm<sup>-1</sup>/atm. Pressure shift values<sup>11</sup> have complicated J" dependencies, but to first order the absolute value of pressure shifts are expected to depend linearly on wavenumber. The HITRAN pressure shift values for the v<sub>3</sub> fundamental band of <sup>12</sup>C<sup>16</sup>O<sub>2</sub> at 2349 cm<sup>-1</sup> are typically about -0.003 cm<sup>-1</sup>/atm. Since our 2v<sub>3</sub> band of <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O is nearly a factor of 2 higher in frequency at 4639 cm<sup>-1</sup>, a typical pressure shift for this band of -0.007 cm<sup>-1</sup>/atm is very reasonable. Our line position measurements have therefore confirmed the HITRAN positions to well within their tabulated uncertainties of 0.001 cm<sup>-1</sup>.

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**Table 1**

<b>Spectrum Number</b>	<b>Path Length (m)</b>	<b>Pressure (Torr)</b>	<b>Temperature (K)</b>	<b>Resolution (cm<sup>-1</sup>)</b>
1	97.04	65.0	297.5	0.012
2	409.82	45.0	297.8	0.012
3	145.16	45.0	298.0	0.012
4	193.28	59.7	298.0	0.012

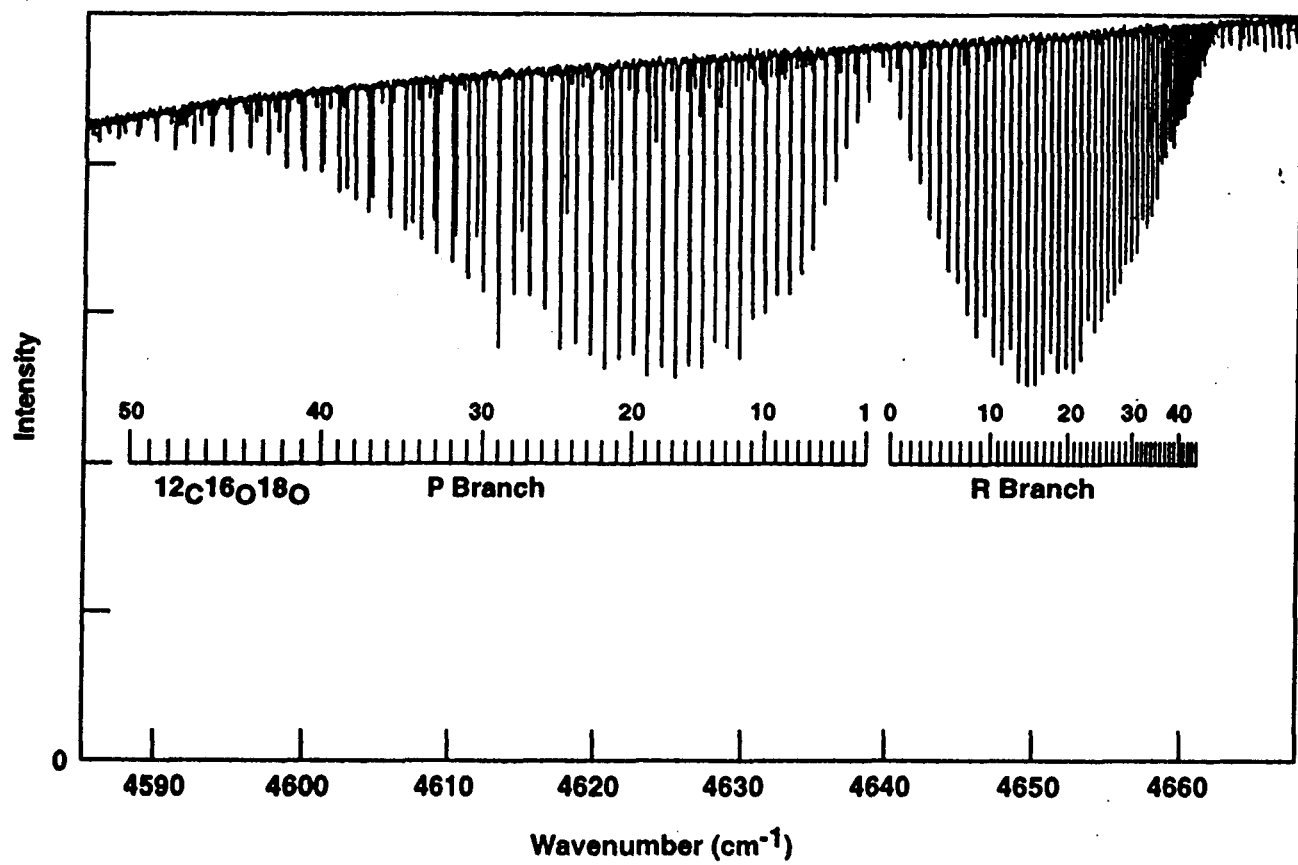


Fig. 1.

TABLE 3

Parameter	
$ R_{\text{vib}} $	$(1.4342 \pm 0.0007) \times 10^{-3} \text{ D}$
<sup>a</sup> $A_1$	$(3.5 \pm 2.0) \times 10^{-5}$
<sup>b</sup> $S_{\text{vib}}^0$	$(0.14416 \pm 0.00014) \times 10^{-22}$

<sup>a</sup>The  $A_1$  Herman-Wallis parameter is dimensionless.

<sup>b</sup>The units of  $S_{\text{vib}}^0$  are  $\text{cm}^{-1}/(\text{molecule}/\text{cm}^2)$  of total  $\text{CO}_2$  at 296 K.